



Letter

Integrating nanostructured electrodes in organic photovoltaic devices for enhancing near-infrared photoresponse



Alexandre M. Nardes^a, Sungmo Ahn^b, Devin Rourke^b, Chenchen Mao^b,
 Jao van de Lagemaat^a, Andrew J. Ferguson^{a,*}, Wounjhang Park^{b,c}, Nikos Kopidakis^{a,d,**}

^a National Renewable Energy Laboratory, 15013 Denver West Parkway, Golden, CO 80401, USA

^b Department of Electrical, Computer, and Energy Engineering, University of Colorado, Boulder, CO 80309-0425, USA

^c Materials Science and Engineering Program, University of Colorado, Boulder, CO 80303, USA

^d Department of Engineering, Macquarie University, NSW, 2109, Australia

ARTICLE INFO

Article history:

Received 1 April 2016

Received in revised form

2 August 2016

Accepted 10 September 2016

Keywords:

Organic photovoltaics

Photonic electrodes

Nanostructured electrodes

Plasmons

Surface plasmon polaritons

ABSTRACT

We introduce a simple methodology to integrate prefabricated nanostructured-electrodes in solution-processed organic photovoltaic (OPV) devices. The tailored “photonic electrode” nanostructure is used for light management in the device and for hole collection. This approach opens up new possibilities for designing photonic active structures that can enhance the absorption of sub-bandgap photons in the active layer. We discuss the design, fabrication and characterization of photonic electrodes, and the methodology for integrating them to OPV devices using a simple lamination technique. We demonstrate theoretically and experimentally that OPV devices using photonic electrodes show a factor of ca. 5 enhancement in external quantum efficiency (EQE) in the near infrared region. We use simulations to trace this observed efficiency enhancement to surface plasmon polariton modes in the nanostructure.

© 2016 Published by Elsevier B.V.

1. Introduction

The development of low bandgap, light-harvesting copolymers has enabled single-junction OPV devices to surpass the 10% power conversion efficiency (PCE) mark [1,2]. Further enhancements of OPV performance are likely to require the design and optimization of device architectures, including the use of multiple junctions [2] and photonic/plasmonic elements [3–5]. The latter opens up the possibility to broaden the spectral response of single-junction OPV due to enhanced light harvesting by weak, sub-bandgap absorptions due to, for instance, charge-transfer (CT) states [6–11]. Sensitive EQE measurements, coupled with the measured optical properties of the device stack, suggest that the *internal* quantum efficiency (IQE) for many OPV active layers remains high (and constant) even at photon energies much smaller than the optical bandgap of the active materials [11]. The observation of efficient

carrier generation from CT states has been suggested as a paradigm-shifting route to a new efficiency regime for OPV [12].

Efforts to exploit photonic/plasmonic elements in OPV devices have included a number of different strategies [3–5]. These include incorporation of metallic nanoparticles into the device architecture or sandwiching the active layer and carrier transport layers in a metallic nanocavity [13,14], which enhance the optical and photovoltaic properties as a result of strong near-field coupling to a localized surface plasmon resonance (LSPR) and/light scattering effects. More recently, research has focused on the use of patterned metal electrodes, which provide a greater degree of control/flexibility and can be designed to couple incident solar radiation into surface plasmon polariton (SPP) modes or waveguide modes that propagate laterally through the active layer [3–5]. There have been several pioneering theoretical [15,16] and experimental [17–22] studies of the incorporation of random and periodic patterned metal electrodes into OPV devices, several of which aim to extend the spectral response of the active layer further into the near-infrared (NIR) [18–22]. Early, pioneering efforts to include such structures demonstrated the viability of such a strategy, but the sub-bandgap EQE enhancement was limited either by use of a non-optimal grating period that resulted in excitation of higher SPP

* Corresponding author.

** Corresponding author. Department of Engineering, Macquarie University, NSW, 2109, Australia.

E-mail addresses: andrew.ferguson@nrel.gov (A.J. Ferguson), nikos.kopidakis@mq.edu.au (N. Kopidakis).

modes [18,20] or the reduced transparency of the nanostructured electrode [19,22].

We have previously shown by a combined optical and electrical simulation of the device performance that NIR photocurrent enhancement can be achieved by using a metal nanograting as the back electrode [16]. Our simulations showed that excitation of SPPs in the grating enhances the optical field in the active layer and that the grating can be designed so that the enhancement occurs in the near-infrared where the normal absorption in the active layer is low [16]. Here we experimentally realize this device and demonstrate that enhancement of the EQE is indeed observed in the spectral region predicted by the simulation. This confirms the power of simulation to design gratings that target optical field enhancement in a specific wavelength range of interest that can be focused in the active layer. We present a methodology for fabricating gratings by laser interference lithography (LIL) and a simple lamination technique for integrating them as back electrodes in an OPV device [23,24]. We demonstrate reasonable sub-bandgap EQE enhancement factors (>2 even for non-optimal incident light polarization) using the prototypical P3HT:PCBM active layer. However, the overall device performance is limited by the need to include an adhesive layer to bond the pre-fabricated grating electrode to the active layer. With that said, we anticipate that this current limitation could be circumvented by the use of a more appropriate adhesive layer, and that the strategy demonstrated here could be universally applied to any OPV active layer.

2. Experimental

The nanostructured-Ag electrodes were fabricated by the LIL technique, which is cost-effective and also scalable to larger volume production [25,26]. First, a 200 nm thick Ag layer was thermally evaporated onto a 125 μm thick polyethylene terephthalate (PET) flexible substrate. A thin photoresist layer was spin coated on top of the Ag film, and exposed under the sinusoidal laser interference pattern formed uniformly over large area by a custom-built Lloyd's interferometer. We used a 325 nm He-Cd laser as a light source with sufficient coherence length. Precise control of the baking, exposure, and development conditions made it possible to obtain one-dimensional grating patterns with slight undercut in the resist layer. A 20 nm thick Ag layer was evaporated on top of the developed photoresist pattern, which, after an acetone lift-off step, resulted in highly uniform one-dimensional Ag gratings over an area of $\sim 1\text{ cm}^2$.

Inverted OPV devices, without a top electrode, had the structure glass/ITO/ZnO/P3HT:PCBM and were fabricated as reported previously [23]. A glass slide with patterned ITO was sonicated in acetone and isopropyl alcohol, and subsequently treated with an oxygen plasma for 5 min. Zinc oxide (ZnO) is deposited by spin coating a diethylzinc solution mixed with tetrahydrofuran, followed by thermal conversion at 120 $^{\circ}\text{C}$ in air. The Glass/ITO/ZnO substrates are transferred to a N_2 -filled glove box for the active layer deposition. The active layer was $\sim 250\text{ nm}$ thick and was spin coated from a 1:1 wt ratio solution of P3HT:PCBM dissolved in dichlorobenzene.

To complete the device, an adhesive layer is required on the nanostructured-Ag/PET substrates [23]. For this we used a P3HT solution in dichlorobenzene with 10% by weight d-sorbitol, spin coated on the nanostructured-Ag surface. The two parts of the device are then brought together and placed in a hydraulic hot press for lamination in air, to complete the device stack: Glass/ITO/ZnO/P3HT:PCBM//P3HT:sorbitol/Ag/PET, where “//” denotes the laminated interface. Both the top and bottom plates of the press are preheated to 130 $^{\circ}\text{C}$. The sample is kept on the bottom plate for 10 min and then pressed with 1.9 MPa for an additional 10 min.

Control devices were fabricated at the same time with the same procedure using flat-Ag electrodes.

The EQE of the devices was measured under short circuit conditions with a Newport Oriel IQE200 system, using lock-in detection.

3. Results and discussion

3.1. Nanostructured electrode design and fabrication

Enhanced NIR photoresponse in OPV devices based on the P3HT:PCBM active layer has been previously demonstrated using quasi-random [19] and periodic [18,21] patterned metal electrodes. In the former case, the overall performance of the device at wavelengths above the optical bandgap is limited by the transmittance of the partially transparent gold layer, whereas the latter employ periodic gratings formed by direct nanoimprint lithography of the active layer, but result in EQE enhancement factors less than 2.5.

Similar to previous work [21], we chose to design a simple, and thus easy to fabricate, nanostructure comprising a periodic surface grating where the SPP mode is positioned in the NIR spectral region. We use the finite element method (FEM) in the commercial package COMSOL Multiphysics to simulate the optical field distribution in the whole device stack. The simulation takes as inputs the n & k spectra of each layer and the solar spectrum, and numerically solves Maxwell's equations for the steady-state electric field profile within the active layer [16]. The thickness of each of the flat layers on the device stack (ITO, ZnO and active layer) is fixed to the experimental values and the parameters that are allowed to vary to tune the position of the SPP resonance are the depth (height), duty ratio, and period of the grating (the linewidth of the grating feature is determined by the product of the duty ratio and grating period). Periodic boundary conditions are imposed (along the x-direction in Fig. 1) in such a way that the two-dimensional simulation cell has width equal to the nanostructured grating periodicity.

Fig. 1a shows the simulated electric field amplitude map of the SPP mode excited at normal incidence at 490 nm (E_y component) for a bare Ag grating in air with the following geometric parameters of the grating: period = 420 nm, duty ratio = 0.64, height = 20 nm. Fig. 1b shows a scanning electron micrograph of the experimental grating fabricated by LIL on a PET substrate. The simulated and experimental reflectance spectra for this grating are shown, along with the reflectance for a flat Ag electrode for comparison, in Fig. 1c. While the flat Ag electrode only exhibits absorption in the ultraviolet, the nanostructured grating electrode shows a clear reflectance dip at 490 nm due to the light coupling into the SPP mode, as shown in Fig. 1a. The good match in the position of the dip between measurement and simulation verifies that the SPP mode is excited on the grating surface as predicted. We note that the dip of the measured reflectance spectrum is shallower than that predicted (see Fig. 1c). We attribute this to the light scattering by the surface and line edge roughness of the fabricated grating, also seen in the micrograph of Fig. 1b, that somewhat diminish the quality and photonic properties of the structure. As we will discuss below, this is also manifested in a measured EQE enhancement that is smaller than predicted theoretically.

3.2. Simulated optical properties of complete device stack

Simulations confirm that the SPP mode of the bare Ag grating shifts to longer wavelengths when a higher index material (namely the active layer of the device in this study) is deposited onto the grating. This results in a SPP mode that is predominantly confined within the active layer (Fig. 2a) and is centered at 875 nm

Download English Version:

<https://daneshyari.com/en/article/5144313>

Download Persian Version:

<https://daneshyari.com/article/5144313>

[Daneshyari.com](https://daneshyari.com)